

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Peters et al

Serial No.: 09/238,851

Examiner: Webb, G.

Filed: 1/27/99

Art Unit: 1751

Docket No.: 5545A

Title: Low Surface Tension, Low Viscosity, Aqueous, Acidic Compositions Containing Fluoride And Organic Polar Solvents For Removal Of Photoresist And Inorganic Etch Residues At Room Temperature

DECLARATION OF R. ROVITO UNDER 37 C.F.R. §1.132

I, Roberto Rovito, declare as follows:

1. I currently am employed by Ashland Specialty Chemical Company, a division of Ashland Inc., as a Senior Applications Engineer where I have worked since February 1, 1999.
2. I was awarded a Bachelor of Science in Chemistry and Mathematics in 1978 from Marietta College in Ohio and a PhD. in Organic Chemistry in 1985 from Temple University in Pennsylvania. I held a post-Doctoral post from 1985-1987 at Stanford University in California.
3. Among my responsibilities are the development of new products and testing of existing products in the semiconductor cleaning area.
4. All of the formulations listed in Exhibit 1 were prepared and titrated in Ashland's laboratory facilities in Easton, Pennsylvania. Formulations labeled as Examples 1-5 correspond to examples 1-5 in US Patent No. 5,972,862. Examples DP-1 and DP-2 are identical except acetic acid was added to DP-2. ACT is an example of a buffered composition within the scope of the claims of the presently claimed invention. Pages 1-2

of Exhibit 1 show calculations for creating one type of buffered solution. Page 3 contains the formulations for various examples. Pages 4-13 are titration curves for the various formulations.

5. I have reviewed the contents of Exhibit 1. The results show the difference between a buffered composition (ACT) and compositions (Examples 1-5, DP1 and DP2) that do not function as buffers. Buffered solutions are those solutions that are capable of maintaining their pH at some fairly constant value even when small amounts of acid or base are added. In general, the effective range for a given buffer is about one pH unit on either side of the pK_a of the acid being used. The most effective buffer, ie., the buffer having the greatest pH range on either side of the pK_a for a given acid is prepared using a 1:1 ratio of protonated and deprotonated forms of a weak acid. An example of such a buffer is the ACT example in Exhibit 1. Simply adding an acid and its conjugate base to a formulation does not create a solution that will function as a buffer. Examples 1-5 from patent 5,972,862 show how formulations that contain both an acid and a base fail to provide a buffered system, ie the formulations cannot maintain a fairly constant pH when small amounts of a base is added. In contrast a buffered composition of the present invention "ACT" maintains a fairly constant pH up to about the addition of 10 ml of 0.1N KOH. It was postulated in a rejection of the present invention that the addition of acetic acid to a composition containing ammonium fluoride would form a buffered solution in situ. Examples DP-1 and DP-2 show that merely adding a weak acid to a formulation does not create a solution able to withstand the addition of small amounts of 0.1N KOH.

6. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: July 15, 2003

Roberto Rovito

Roberto Rovito

0307sdec312

EXHIBIT 1

Technical description of a buffered solution

Formulations for examples 1-5, DP-1, DP-2 and ACT

Titration curves for the formulations

Using a Weak Acid to Create a Buffered Solution

For a weak acid: $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$, and the equilibrium constant is k_a

$$\text{where } k_a \equiv [\text{H}^+] [\text{A}^-]/[\text{HA}]$$

$$\log k_a = \log [\text{H}^+] + \log [\text{A}^-] - \log [\text{HA}]$$

$$-\log k_a = -\log [\text{H}^+] - \log [\text{A}^-] + \log [\text{HA}]$$

$$-\log k_a \equiv p_{k_a}$$

$$-\log [\text{H}^+] \equiv \text{pH}$$

$$\text{hence, } p_{k_a} = \text{pH} - \log [\text{A}^-] + \log [\text{HA}]$$

$$\text{and pH} = p_{k_a} + \log [\text{A}^-] - \log [\text{HA}]$$

$$\text{or pH} = p_{k_a} + \log ([\text{A}^-]/[\text{HA}])$$

if $[\text{A}^-]/[\text{HA}]$ is < 1 , then $\text{pH} < p_{k_a}$

if $[\text{A}^-]/[\text{HA}] = 1$, then $\text{pH} = p_{k_a}$

if $[\text{A}^-]/[\text{HA}]$ is > 1 , then $\text{pH} > p_{k_a}$

EXAMPLE #1

Propionic Acid	1.00
Amm. Fl. Anhydr.	8.00
Dimethyl Formamide	40.00
TMAF 25%	20.00
EP-120A	0.10
DI Water	30.90
pH = 5.04	

EXAMPLE #4

Acetic Acid	0.10
Amm. Fl. Anhydr.	10.00
Dimethyl Formamide	45.00
TMB-C	3.00
EP-120A	0.10
pH = 5.45	

DP1

DMAC	67.5
DI Water	30.0
NH4F (40%)	2.5
Acetic Acid (glac.)	0.0

DP2

DMAC	65.5
DI Water	30.0
NH4F (40%)	2.5
Acetic Acid (glac.)	2.0
pH = 4.75	

ACT

DMAC	57.5
Ammonium Acetate	15.6
Acetic Acid (glac.)	12.0
DI Water	12.4
Amm. Floride (40%)	2.5

EXAMPLE #3

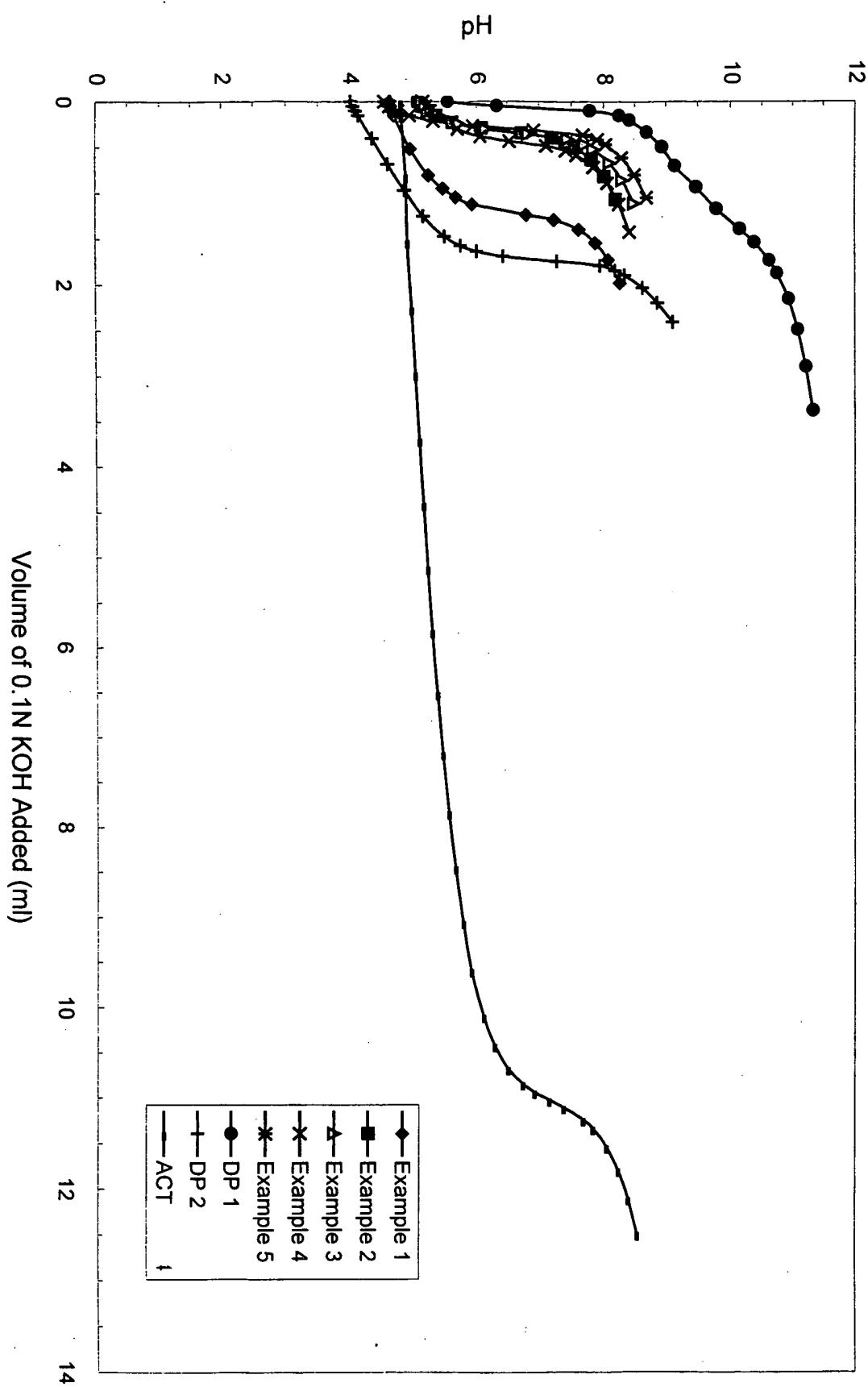
Isobutyric Acid	0.20
Amm. Fl. Anhydr.	5.00
DMAC	35.00
TMAF 25%	40.00
EP-120A	0.10
DI Water	0.10
Formamide	40.00
pH = 5.42	

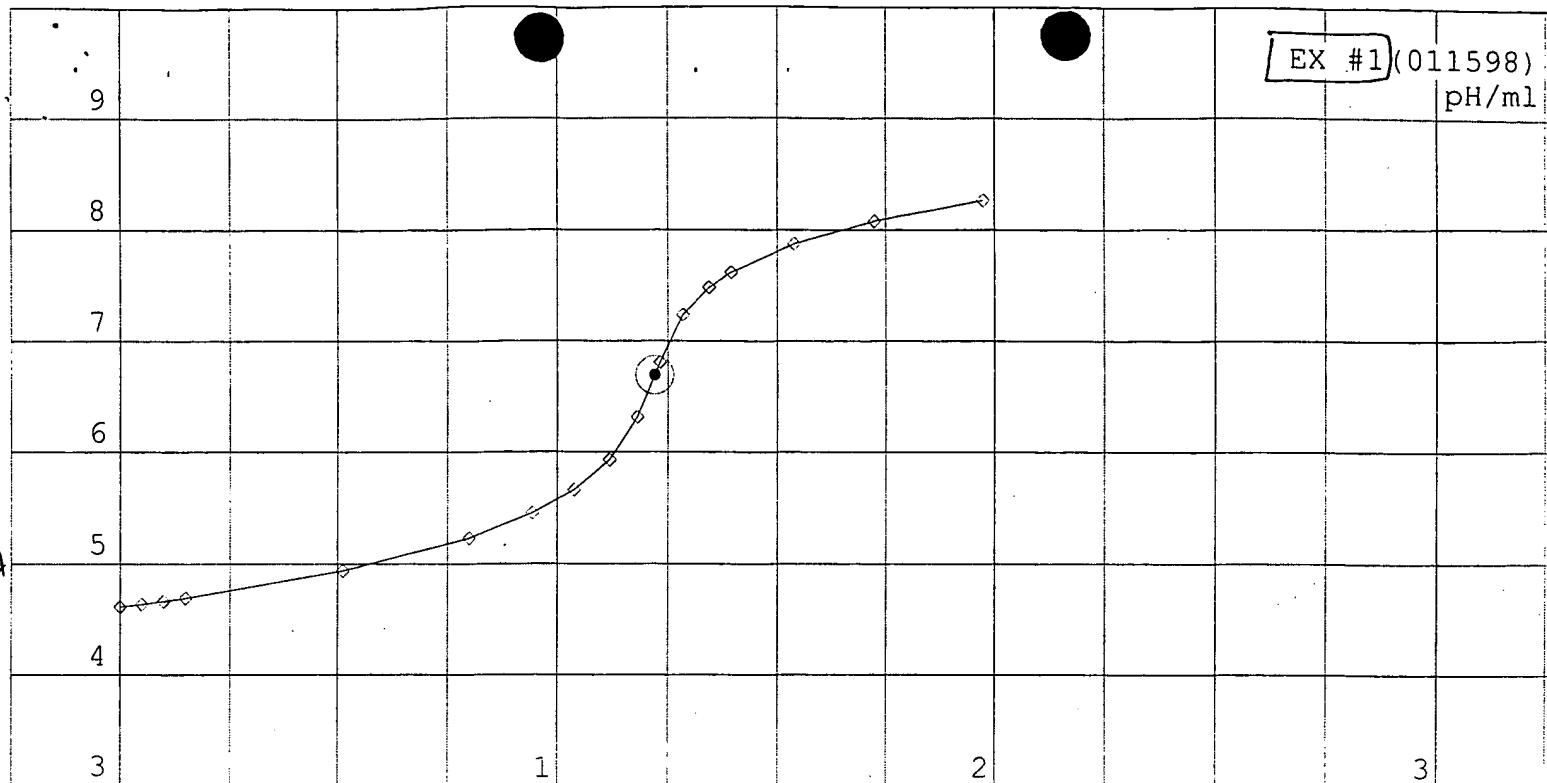
EXAMPLE #5

Amm. Fl. Anhydr.	1.00
Dimethyl Formamide	69.00
DI Water	29.00
Boric Acid	0.30

DMAC - Dimethylacetamide
TMAF - Tetramethylammonium formate
TMBF - Tetramethylammonium acetate
EP-120A - Is a poly(oxyethylene)phenylester from Dai-ichi Kogyo Seiyaku Co., Ltd.

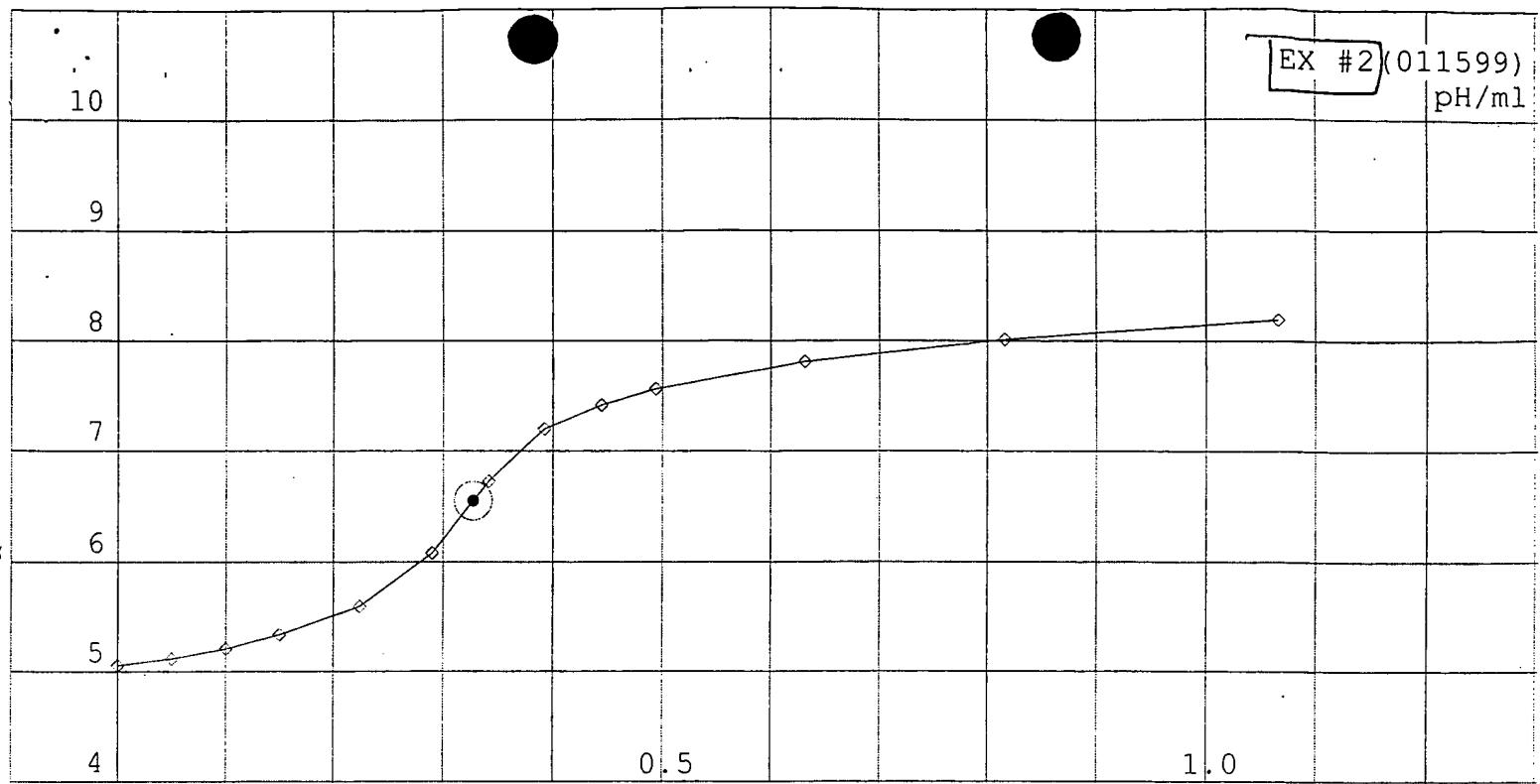
Titration Curves for Various Formulations





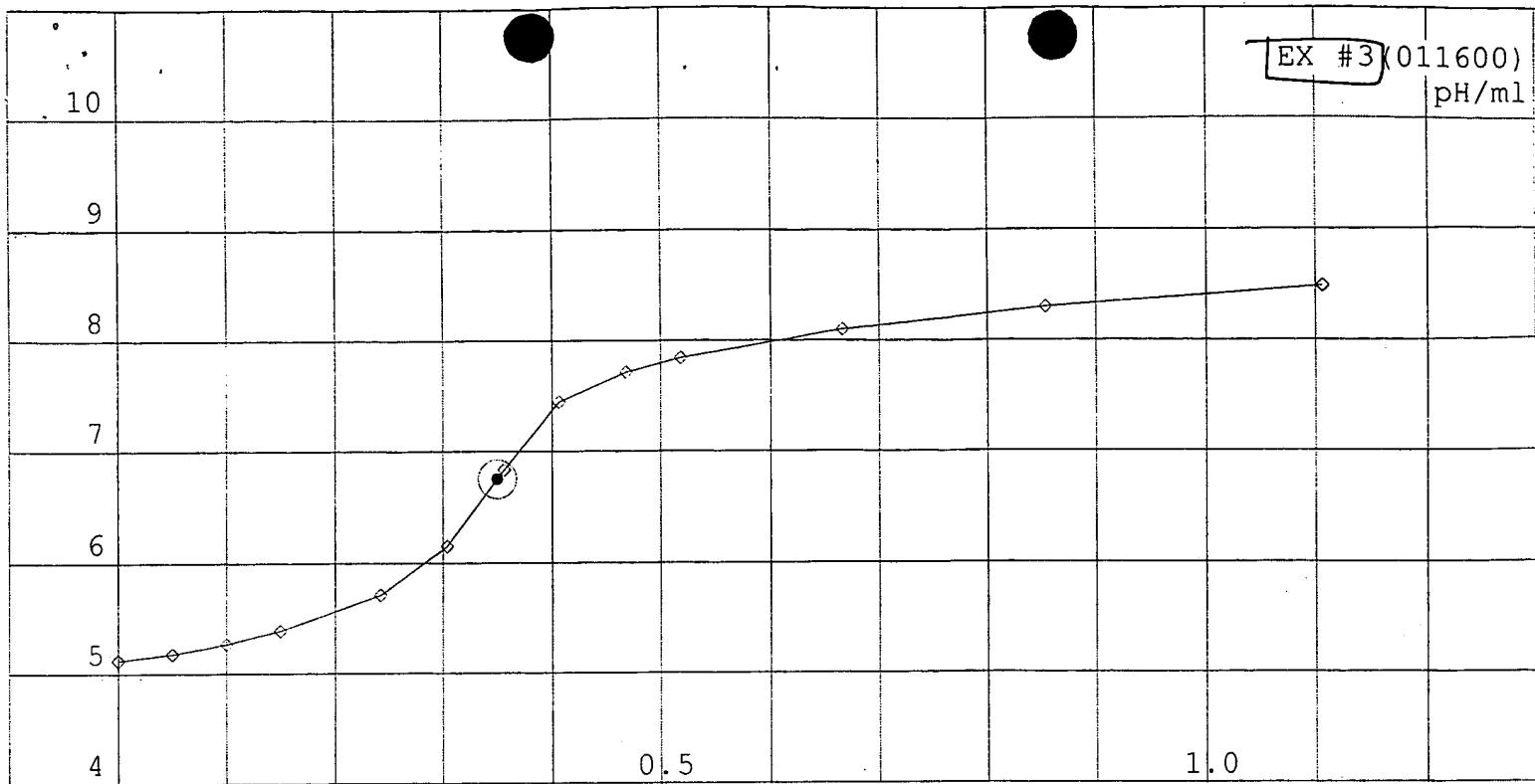
'fr
 751 GPD Titrino 09140 751.0020 titrant
 date 2001-03-21 time 10:38 215 0.1% KOH
 card label:Appl.751
 pH(init) 4.61 DET pH NE14PA
 smpl size 0.5061 id#1 EX #1
 EP1 1.220 ml 6.69
 stop #EP reached
 device label Titrino sign:JE
 =====

'mp
 751 GPD Titrino 09140 751.0020
 date 2001-03-21 time 10:38 215
 pH(init) 4.61 DET pH NE14PA
 smpl size 0.5061 id#1 EX #1
 [V/ml] [pH] T/°C ERC
 0.0000 4.615 0.0
 0.0500 4.637 13.2
 0.1000 4.665 16.1
 0.1500 4.693 18.3
 0.5120 4.940 23.4
 0.8000 5.231 31.5
 0.9440 5.454 40.7
 1.0380 5.662 51.1
 1.1180 5.931 60.6
 1.1800 6.314 65.9
 1.2320 6.806 66.9
 1.2840 7.238 63.7
 1.3440 7.484 55.7
 1.3940 7.620 44.9
 1.5380 7.876 34.5
 1.7240 8.079 0.0
 1.9740 8.262 0.0
 =====



'fr
 751 GPD Titrino 09140 751.0020 titrant: 0.1N KOH
 date 2001-03-21 time 10:43 216
 card label:Appl.751
 pH(init) 5.05 DET pH NE14PA
 smpl size 0.5713 id#1 EX #2
 EP1 0.328 ml 6.55
 stop #EP reached
 device label Titrino sign: JE
 =====

'mp
 751 GPD Titrino 09140 751.0020
 date 2001-03-21 time 10:43 216
 pH(init) 5.05 DET pH NE14PA
 smpl size 0.5713 id#1 EX #2
 [V/ml] [pH] T/°C ERC
 0.0000 5.055 0.0
 0.0500 5.118 34.1
 0.1000 5.209 44.0
 0.1500 5.337 53.5
 0.2240 5.596 63.2
 0.2900 6.082 68.3
 0.3420 6.728 68.9
 0.3920 7.198 65.4
 0.4440 7.416 56.9
 0.4940 7.560 45.8
 0.6320 7.809 35.0
 0.8160 8.011 0.0
 1.0660 8.195 0.0
 =====

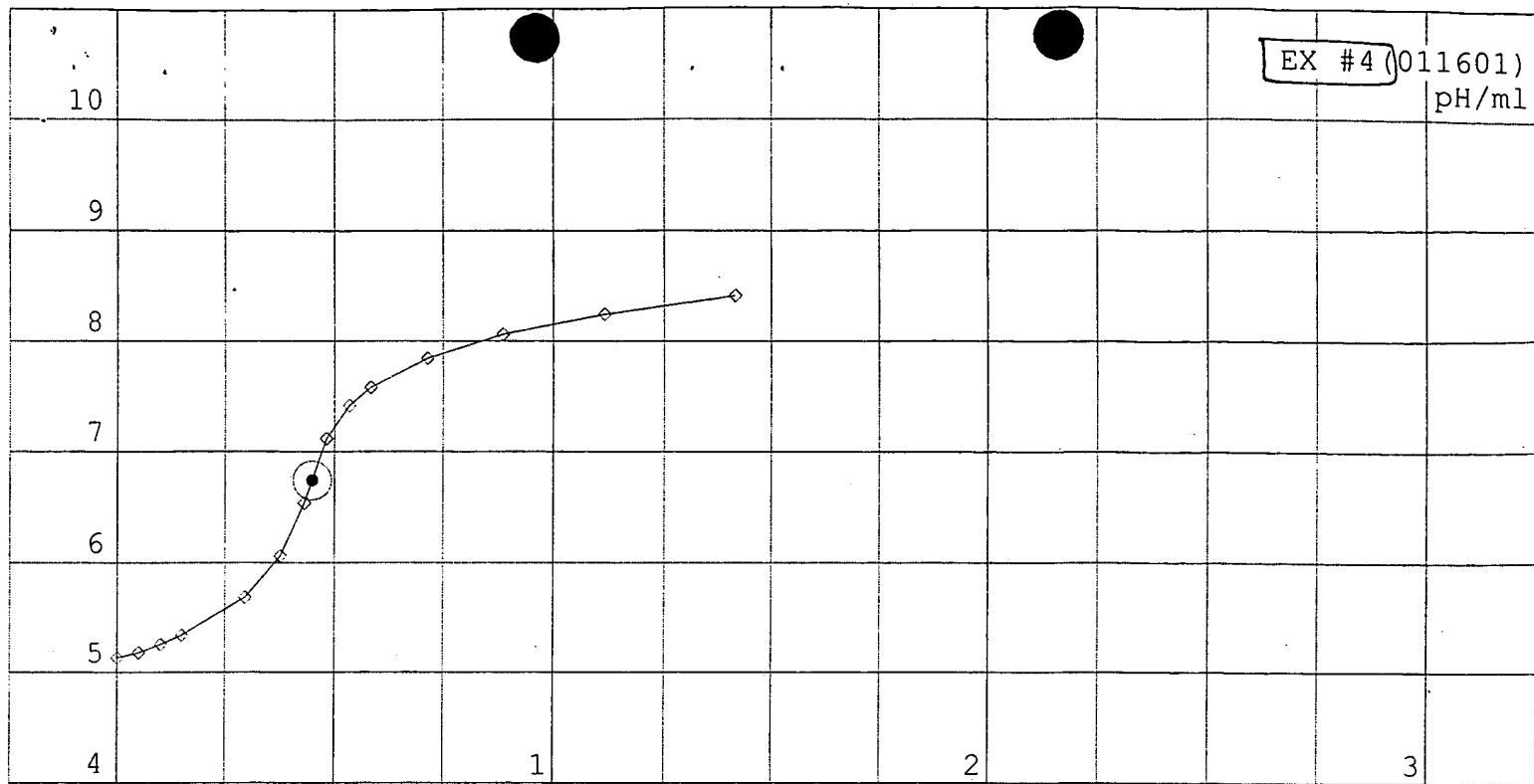


'fr
 751 GPD Titrino 09140 751.0020
 date 2001-03-21 time 10:48 217
 card label:Appl.751
 pH(init) 5.12 DET pH NE14PA
 smpl size 0.5739 id#1 EX #3
 EP1 0.350 ml 6.75
 stop #EP reached
 device label Titrino sign: JE
 =====

titrant: 0.1N KOH

'mp
 751 GPD Titrino 09140 751.0020
 date 2001-03-21 time 10:48 217
 pH(init) 5.12 DET pH NE14PA
 smpl size 0.5739 id#1 EX #3
 [V/ml] [pH] T/°C ERC
 0.0000 5.121 0.0
 0.0500 5.178 33.1
 0.1000 5.270 43.2
 0.1500 5.388 52.9
 0.2420 5.714 63.1
 0.3040 6.151 68.8
 0.3560 6.832 70.1
 0.4060 7.444 67.2
 0.4680 7.712 58.1
 0.5180 7.842 44.6
 0.6660 8.099 33.9
 0.8540 8.301 0.0
 1.1060 8.489 0.0
 =====

EX #3 (011600)
pH/ml

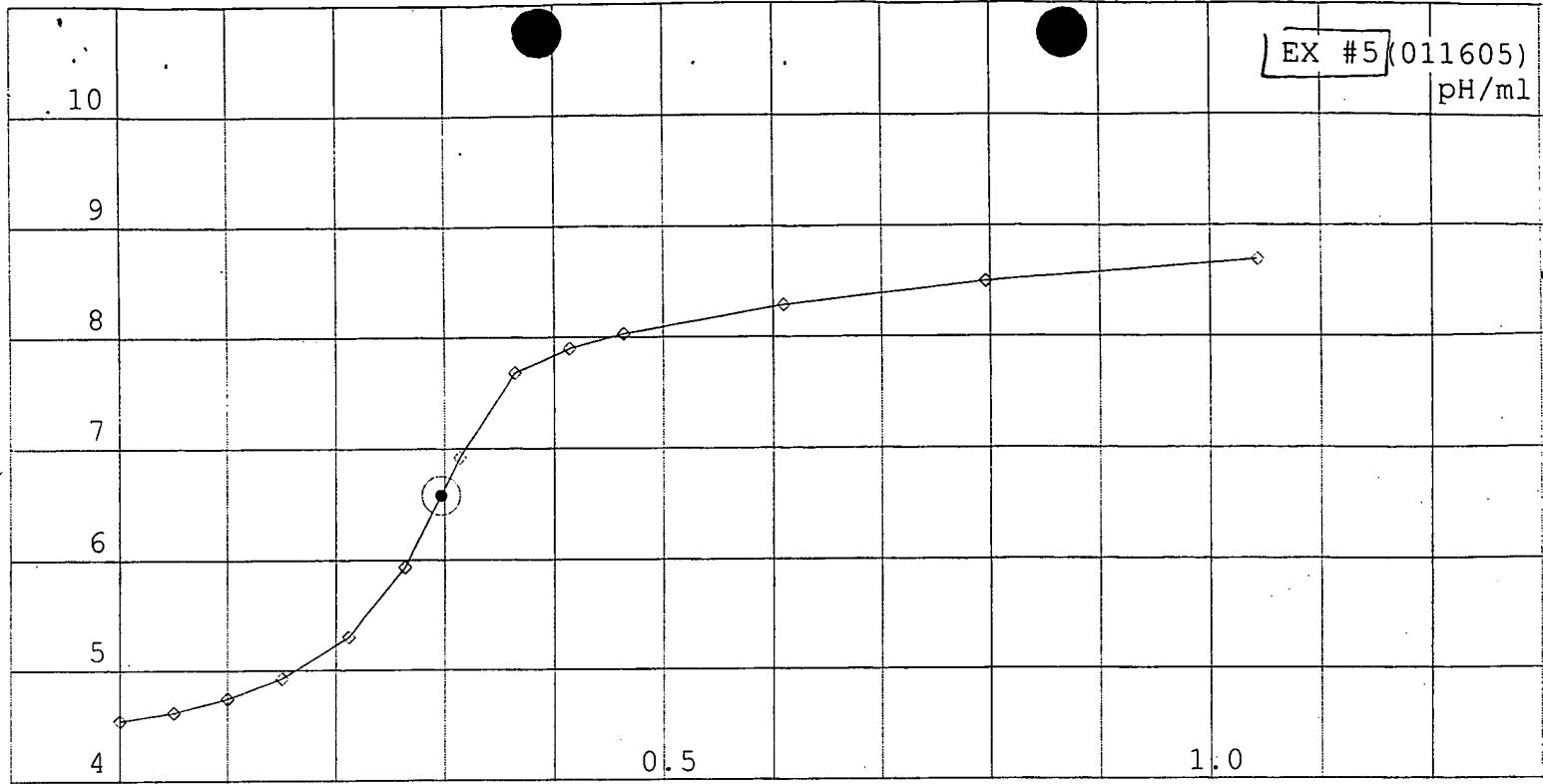


'fr
 751 GPD Titrino 09140 751.0020
 date 2001-03-21 time 10:54 218 titrant: 0.1N KOH
 card label:Appl.751
 pH(init) 5.13 DET pH NE14PA
 smpl size 0.5613 id#1 EX #4
 EP1 0.450 ml 6.74
 stop #EP reached
 device label Titrino sign: JE
 =====

'mp
 751 GPD Titrino 09140 751.0020
 date 2001-03-21 time 10:54 218
 pH(init) 5.13 DET pH NE14PA
 smpl size 0.5613 id#1 EX #4

V/ml	pH	T/°C	ERC
0.0000	5.131		0.0
0.0500	5.179		28.2
0.1000	5.253		36.3
0.1500	5.339		44.5
0.2960	5.684		56.2
0.3780	6.061		65.0
0.4320	6.539		68.2
0.4820	7.116		67.0
0.5340	7.414		60.8
0.5840	7.579		49.7
0.7140	7.843		38.0
0.8860	8.060		27.5
1.1160	8.246		0.0
1.4160	8.415		0.0

 =====



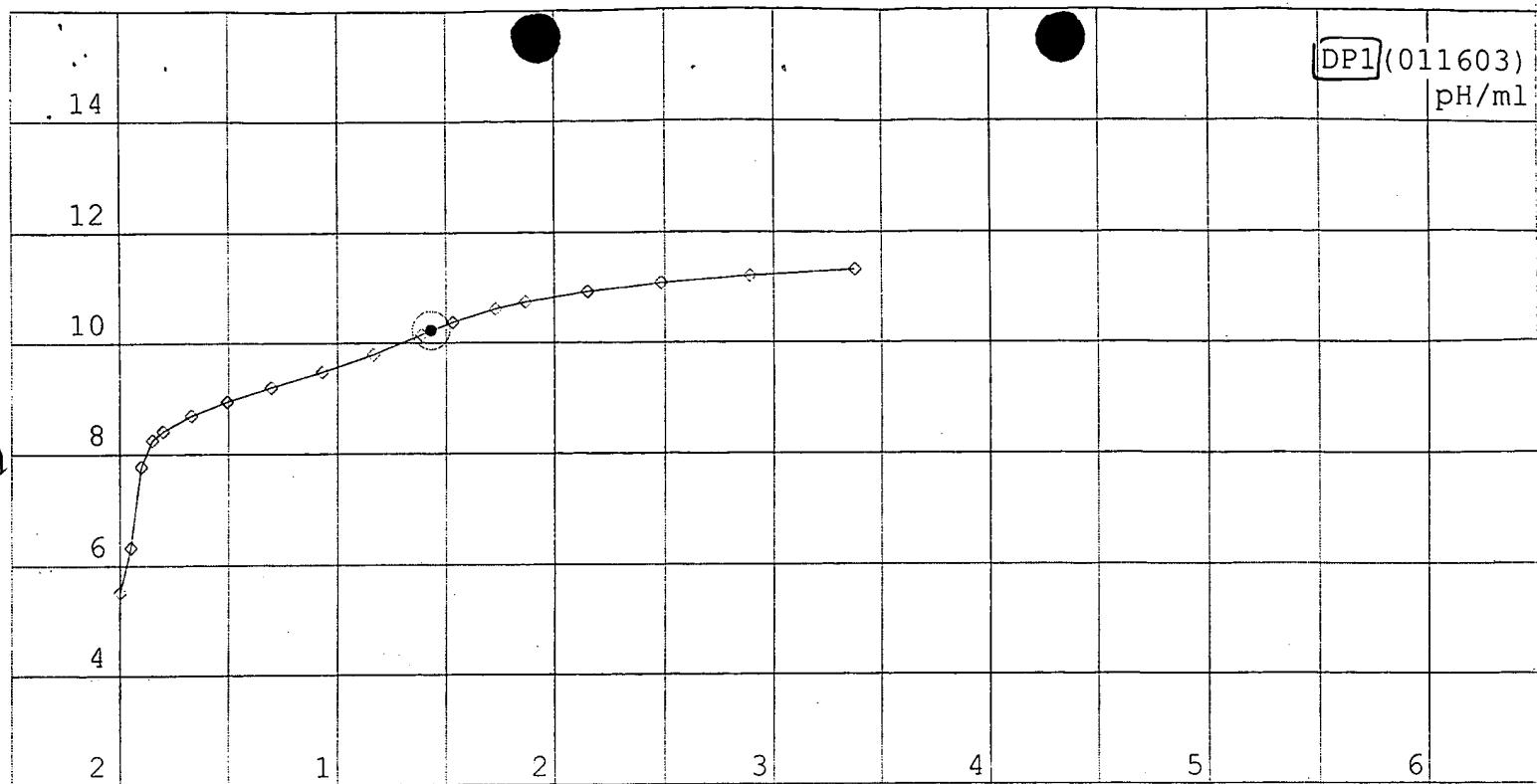
'fr
 751 GPD Titrino 09140 751.0020
 date 2001-03-21 time 13:21 222
 card label:Appl.751
 pH(init) 4.55 DET pH NE14PA
 smpl size 1.3935 id#1 EX #5
 EP1 0.297 ml 6.58
 stop #EP reached
 device label Titrino sign: JE
 =====

titrant
O·INKOH

'mp
 751 GPD Titrino 09140 751.0020
 date 2001-03-21 time 13:21 222
 pH(init) 4.55 DET pH NE14PA
 smpl size 1.3935 id#1 EX #5

V/ml	pH	T/°C
0.0000	4.543	0.0
0.0500	4.618	40.7
0.1000	4.743	52.4
0.1500	4.924	62.0
0.2120	5.302	69.1
0.2640	5.936	72.4
0.3140	6.920	72.7
0.3640	7.679	69.4
0.4140	7.898	59.7
0.4640	8.030	45.0
0.6100	8.289	34.6
0.7960	8.496	0.0
1.0440	8.693	0.0

 =====

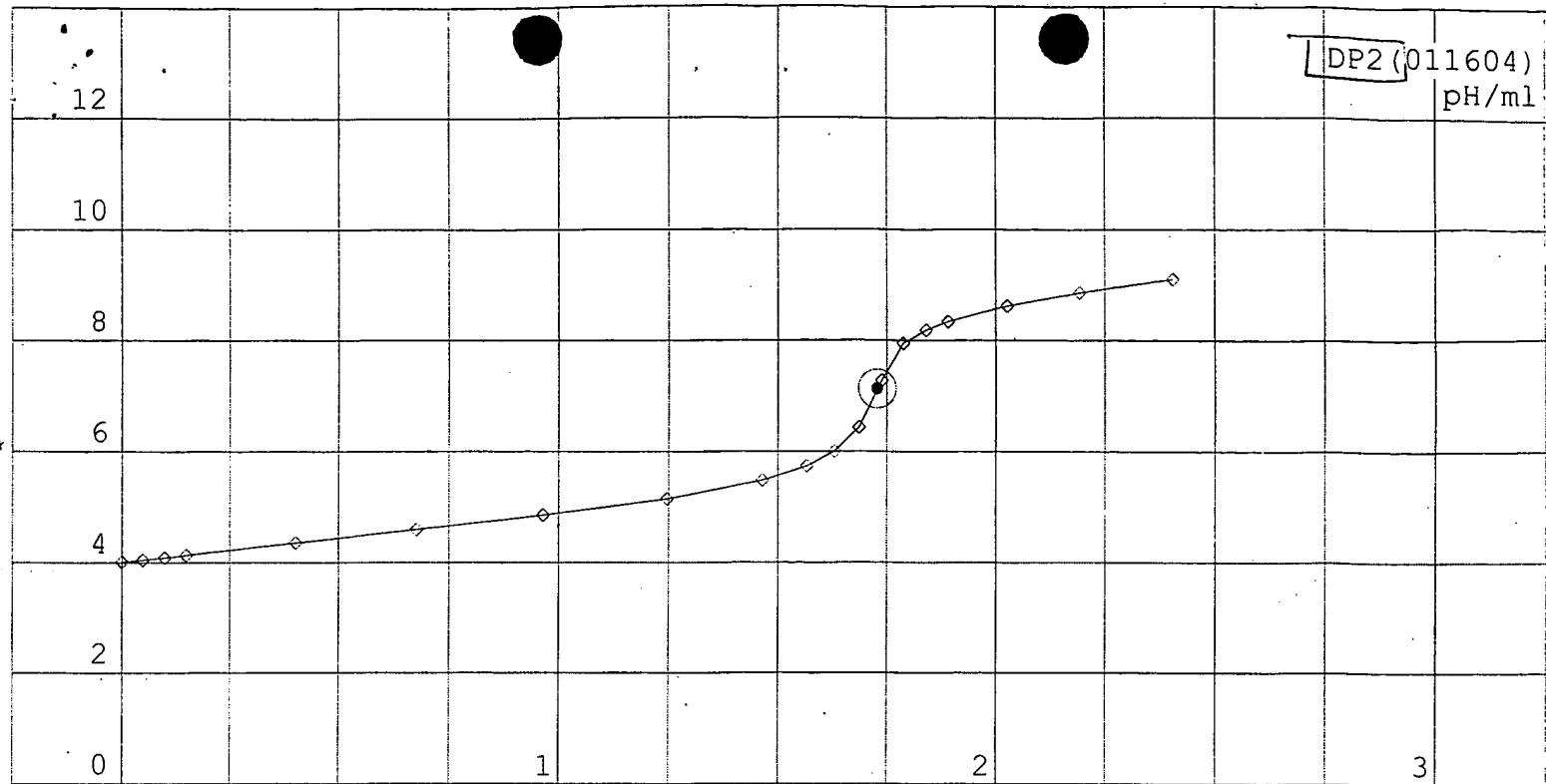


DP1 (011603)
pH/ml

'fr
 751 GPD Titrino 09140 751.0020
 date 2001-03-21 time 11:06 220
 card label:Appl.751
 pH(init) 5.70 DET pH NE14PA
 smpl size 0.5318 id#1 DP1
 EP1 1.432 ml 10.22
 stop #EP reached
 device label Titrino sign: JE
 =====

titrant: 0.1N KOH

'mp
 751 GPD Titrino 09140 751.0020
 date 2001-03-21 time 11:06 220
 pH(init) 5.70 DET pH NE14PA
 smpl size 0.5318 id#1 DP1
 V/ml pH T/°C ERC
 0.0000 5.519 0.0
 0.0500 6.328 73.8
 0.1000 7.780 73.3
 0.1500 8.243 67.8
 0.2000 8.407 53.3
 0.3300 8.689 40.7
 0.4940 8.940 33.7
 0.6980 9.193 30.7
 0.9300 9.472 31.3
 1.1660 9.791 33.7
 1.3860 10.146 34.6
 1.5300 10.372 32.2
 1.7280 10.619 27.1
 1.8660 10.741 21.2
 2.1500 10.931 16.0
 2.4840 11.083 11.7
 2.8920 11.213 0.0
 3.3740 11.330 0.0
 =====

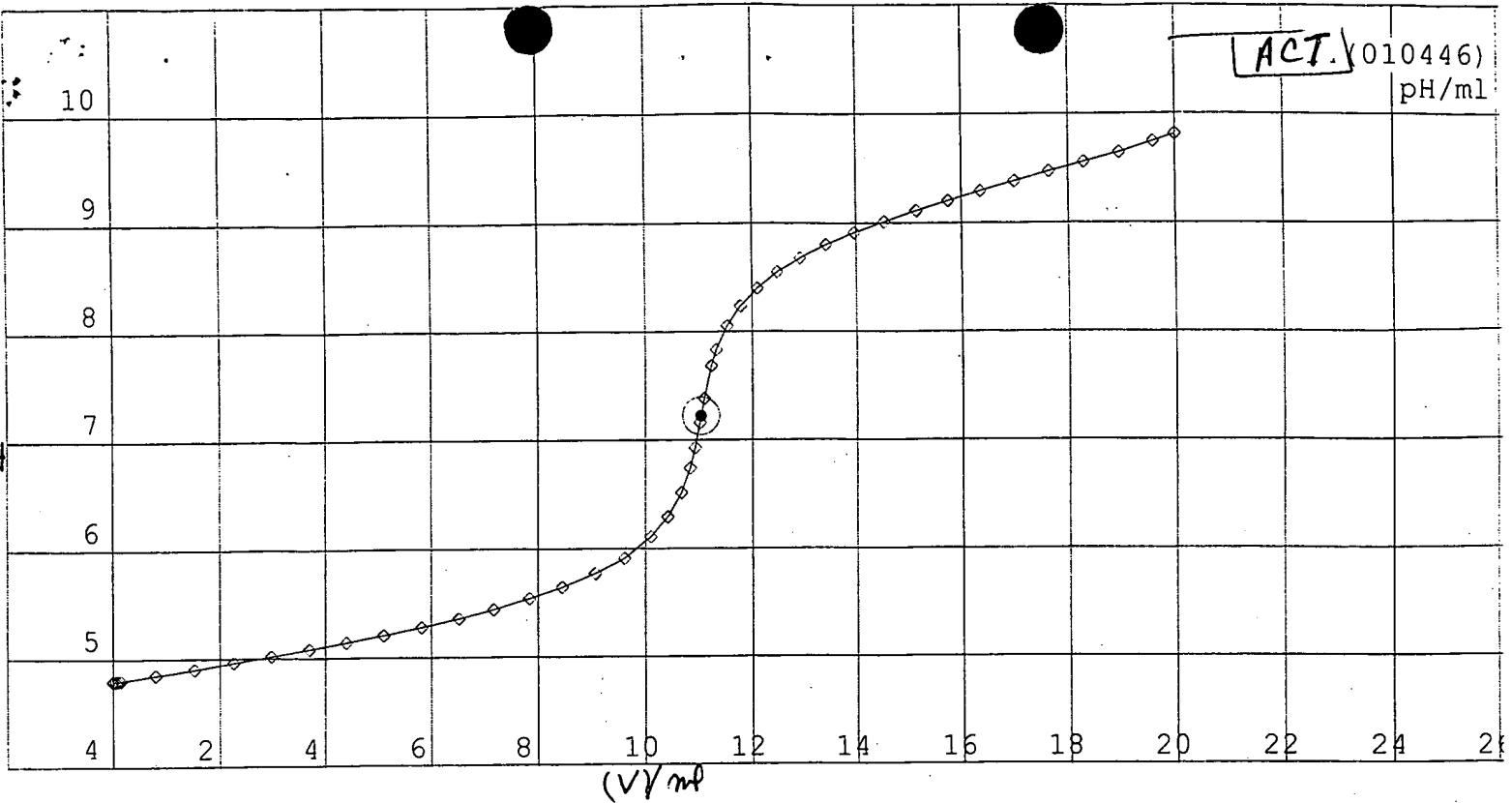


'fr
 751 GPD Titrino 09140 751.0020
 date 2001-03-21 time 11:12 221 titrant: 0.1N KOH
 card label: Appl.751
 pH(init) 4.01 DET pH NE14PA
 smpl size 0.554 id#1 DP2
 EP1 1.728 ml 7.12
 stop #EP reached
 device label Titrino sign: JE
 =====

'mp
 751 GPD Titrino 09140 751.0020
 date 2001-03-21 time 11:12 221
 pH(init) 4.01 DET pH NE14PA
 smpl size 0.554 id#1 DP2

V/ml	pH	T/°C	ERC
0.0000	4.013		0.0
0.0500	4.046		18.7
0.1000	4.087		22.6
0.1500	4.133		23.4
0.4000	4.356		23.2
0.6780	4.598		23.5
0.9640	4.854		26.0
1.2460	5.147		32.6
1.4640	5.478		43.2
1.5660	5.739		54.8
1.6300	6.004		65.0
1.6860	6.433		70.3
1.7380	7.277		71.3
1.7880	7.945		68.4
1.8400	8.188		59.9
1.8900	8.338		48.2
2.0260	8.628		39.4
2.1920	8.867		0.0
2.4040	9.109		0.0

 =====



mp
 751 GPD Titrino JE
 /date 2001-02-16 time 09140 751.0020
 80

pH(init) 4.79 DET pH NE14
 smpl size 0.5549 in id#1 NE-14
 ~60 ml H₂O pH T/°C ERC

0.0000	4.792	0.0
0.0500	4.793	1.7
0.1000	4.795	2.4
0.1500	4.799	2.6
0.8100	4.847	2.6
1.5260	4.901	2.6
2.2560	4.961	2.6
2.9740	5.018	2.7
3.6980	5.081	2.8
4.4080	5.144	2.9
5.1160	5.209	3.1
5.8200	5.280	3.4
6.5100	5.360	3.8
7.1760	5.442	4.3
7.8360	5.541	5.0
8.4520	5.645	5.9
9.0540	5.772	7.4
9.5940	5.910	10.1
10.0980	6.110	14.2
10.4200	6.293	20.4
10.6780	6.514	28.7
10.8420	6.744	37.3
10.9360	6.930	43.8
11.0240	7.158	46.8
11.1060	7.382	45.5
11.2400	7.685	40.0
11.3360	7.833	32.1
11.5380	8.052	24.3
11.7900	8.237	17.9
12.1060	8.400	13.4
12.4900	8.549	10.3

titrant used: 0.1N KOH

12.9320	8.678	8.3
13.4320	8.803	6.9
13.9640	8.911	6.0
14.5360	9.013	5.4
15.1340	9.114	4.9
15.7420	9.205	4.6
16.3700	9.292	4.4
17.0120	9.382	4.3
17.6520	9.470	4.3
18.2940	9.557	4.3
18.9400	9.644	4.5
19.5860	9.743	0.0
20.0000	9.809	0.0

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